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Photooxidation in Presence of UO_2^{2+} and Molybdate*

WILLIAM MOONEY, GÉRARD FOLCHER

IRDI - DPC/SCM, LA 331 - CEA - Centre d'Etudes Nucléaires de Saclay, 91191 Gif sur Yvette Cédex, France

and CHARLES GIANNOTTI

Institut de Chimie des Substances Naturelles, CNRS, 91190 Gif sur Yvette Cédex, France

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Abstract

Cyclohexene was photooxidized catalytically by the uranyl ion using visible light in the presence of polymolybdate(VI) species in aqueous acid at pH 1 under aerobic conditions. The uranyl ion is the photoactive species and the polymolybdate(VI) serves as the ultimate electron acceptor. The reaction proceeds with formation of a deep-blue, mixed-valence polymolybdate(VI/V) species.

Introduction

Interest in the potential photooxidizing power and photophysics of the uranyl ion, UO_2^{2+}, has inspired numerous studies during the last fifteen years [1]. Special attention was focused on the ability of the ion to photooxidize a wide variety of organic compounds [2, 3] in aqueous solution. However, the majority of these organic compounds are already 'oxidized' in that they contain oxygen-based functionalities (*e.g.*, alcohols, aldehydes and carboxylic acids). The oxidation of alkenes or aromatic compounds was not observed in early experiments [1b], even though both these types of molecules strongly quenched the uranyl fluorescence [2b, 3a]. This phenomenon was explained by invoking the 'physical quenching' of the fluorescence via an uranyl–substrate exciplex which is deactivated without formation of permanent products.

Since the early 1970's, one case of alkene photooxidation by the uranyl ion has been reported [4]. In this system, UO_2^{2+} photocatalyzed the formation of β-hydroxyperoxides from alkenes in aerobic pyridine solutions. The generation and subsequent reaction of hydroxy and superoxide radicals were invoked to explain the products found and the catalytic nature of the process, despite the lack of direct evidence for radical pathways involving these two species. Importantly, an isotopic study of the sources of the oxygen found in the final products revealed that 67% of the hydroxy oxygens came from water in the solvent, whereas 90% of the peroxide oxygens came from molecular oxygen.

Our interest has been to re-explore the photooxidation of alkenes by UO_2^{2+} in order to discover new approaches to this problem. We chose to work with the uranyl ion in aqueous acid in the presence of polymolybdate ion, having observed that the deep-blue, reduced form of the polymolybdate appeared during irradiation of a uranyl/polymolybdate solution containing cyclohexene. Our reasoning was that an anionic but highly oxidized species, like Mo(VI) in a polymolybdate anion, could modify the uranyl ion's solution environment without quenching the excited state, thus actualizing its oxidizing power.

Experimental

Uranyl nitrate hexahydrate (Labosi) and sodium molybdate dihydrate (Merck) were reagent grade and were used as received. Cyclohexene and 1,3-cyclohexadiene were Fluka *puriss.* grade and were used as received. Water was singly distilled. All other chemicals and solvents were reagent grade or better and were used as received.

A typical photolysis experiment was accomplished as follows: from a stock solution of 1×10^{-2} M UO_2^{2+} with pH = 1 and a stock solution of 4×10^{-2} M Na_2MoO_4 with pH = 1 was made 50 ml of a sample solution for which $[UO_2^{2+}] = 4–8 \times 10^{-3}$ M, $[Mo(VI)] = 8–16 \times 10^{-3}$ M, and pH = 1.0. All pH adjustments were made with sulfuric acid and a pH meter (Tacussel TS 70/N). The solution was then made 1–2 mM in cyclohexene by addition of small amounts (5–10 μl) of the liquid with a microliter syringe. After thorough mixing, 3 ml of solution were transferred to a 1 cm-square Pyrex cell equipped with a magnetic stirrer and the cell was capped. Irradiations were then performed at room temperature with a Schoeffel 1000 W mercury–xenon arc lamp

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equipped with a 20 cm-thick aqueous $CuSO_4$ solution filter in a Pyrex vessel which passed visible light in the range 330 nm $<\lambda<$ 700 nm. When it was desirable to perform irradiations under anaerobic conditions rather than the normal aerobic conditions, argon gas (Argon U) was bubbled vigorously through the solution with stirring for at least 30 min in a special cell equipped with a septum cap. An argon blanket was maintained over the solution during the photolysis. Evaporated cyclohexene was replenished by adding 2–3 μl to the cell with a microliter syringe. UV-Vis spectra were taken before and after irradiation using a Perkin–Elmer Lambda 5 spectrophotometer. Stern–Volmer results and fluorescence spectra were obtained using a Perkin–Elmer LS-5 spectrofluorimeter.

Results

The acidification of normal molybdate solutions to pH 1 causes the MoO_4^{2-} molecules to condense into polymolybdate species [5], with concomitant changes in the UV-Vis spectra [6, 7] and redox properties [8]. In our case, the polymolybdate(VI) species possessed a very broad and intense absorption in the ultraviolet range roughly centered at around 250 nm with a long tail extending out to about 400 nm. The polymolybdate(VI) so produced could be reduced by addition of $Na_2S_2O_4$, Zn granules or UCl_4 to the acidic solution. When partially reduced in this manner, the solution became deep-blue in color and exhibited a broad absorption maximum at 780 ± 30 nm, with a shoulder at 620 nm. The maximum changed during the initial stages of the reduction, but was relatively stable after about 1 h. The intensity of the absorption of the reduced solution decreased upon standing in the dark; the loss corresponds to about 20–30% of the original intensity over 1 day, most of which occurs during the first hour.

In the presence of significant concentrations of UO_2^{2+} ($[UO_2^{2+}] \geqslant 5 \times 10^{-3}$ M), normal molybdate solutions with $[Mo(VI)] > 1 \times 10^{-3}$ M produce a yellow uranyl precipitate unless the pH is below 2. We thus decided to work in sulfuric acid media at pH 1.

Illumination of an uranyl/polymolybdate(VI) sample solution at pH 1 under aerobic conditions with visible light brought about a very small increase ($A < 0.03$) in the solution absorption between 650 nm and 850 nm after more than 1 h of irradiation. However, when cyclohexene was added to the solution, illumination caused a blue coloration to appear within several minutes (Fig. 1), and after 1 h of irradiation the solution had become deep-blue. UV-Vis spectra showed a broad absorption between 725 and 825 nm and a shoulder near 620 nm. The maximum changed with time but became stable after about 1 h, finally remaining in the range of 780 ± 30 nm. In addition, although the solution remained blue for days, a loss of absorption intensity accompanied the shifting of the maximum. This loss corresponded to 25 - 50% of the original absorption intensity. Difference spectra, calculated by subtracting a spectrum of the sample taken 1 h after photolysis from one taken immediately after photolysis, revealed the presence of a species with an absorption maximum at 750 nm ± 20 nm which disappears with time under aerobic conditions (Fig. 2). Exclusion of oxygen from the solution retards the formation of the blue species.

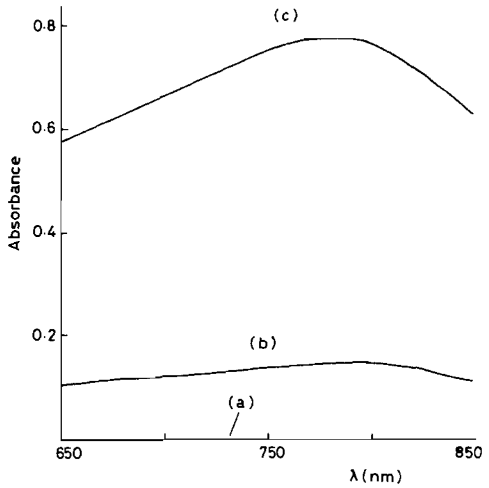

Fig. 1. Absorption spectra of an aerobic solution containing 4.12×10^{-3} M UO_2^{2+}, 1.6×10^{-2} M Mo(VI), pH = 1, during irradiation: (a) the solution before irradiation, (b) after 10 min of irradiation, (c) after 30 min of irradiation.

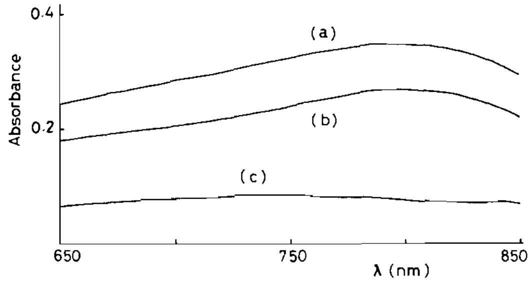

Fig. 2. Spectra of an irradiated sample solution with 8.12×10^{-3} M UO_2^{2+}, 8.08×10^{-3} M Mo(VI) and pH = 1 taken at intervals after irradiation: (a) immediately after 40 min of irradiation, (b) 45 min after irradiation, (c) the difference spectrum, (a) - (b).

ESR analysis provided spectra and *g* values similar to those observed by Yamase and co-workers in reduced and/or photolyzed polymolybdate(VI) systems [7a, 9].

The concentration of UO_2^{2+}, as measured by its UV-Vis absorption spectrum centered at 415 nm, does not decrease during the photolysis. The production of the blue species does not occur under our reaction conditions unless both metal compounds are present with cyclohexene and the solution is irradiated. The blue species can be produced with other organic compounds; for example, 1,3-cyclohexadiene and 2-propanol are also reactive substrates.

Though the reaction products have not been identified, preliminary NMR and IR spectra indicate that the alkene species are oxidized and that exhaustive photolysis produces CO_2.

A series of comparative Stern–Volmer studies were also undertaken to measure the quenching of the uranyl flouorescence in the presence and absence of polymolybdate(VI). The polymolybdate(VI) does not quench the UO_2^{2+} fluorescence. Cyclohexene strongly quenches the fluorescence in all cases, although it is less efficient in the presence of polymolybdate(VI). Thus, $K_{sv} = 5.17 \times 10^3$ M^{-1} for quenching of UO_2^{2+} alone, whereas $K_{sv} = 4.11 \times 10^3$ M^{-1} in the presence of polymolybdate(VI) (Fig. 3). Both plots are linear up to the limit of solubility of cyclohexene in the solutions. Quenching by 2-propanol, in contrast, has virtually the same efficiency in both cases ($K_{sv} \approx 250$ M^{-1}), and the plots are linear.

Discussion

Consideration of our data and comparison with literature results lead us to conclude that the blue species is a mixture of polymolybdate 'mixed-valence' compounds containing reduced Mo(V) centers along with the remaining Mo(VI) centers. The mixed-valence nature of the compound is responsible for the color [10]; completely reduced polymolybdate(V) solutions are yellow [8b]. Furthermore, these species are known to condense even further once reduced [11]; this accounts in part for the shifting of the absorption maximum and the wide range of observed peaks which lead to the uncertainty in the λ_{max} values. The breadth of the peak itself creates an uncertainty of ±10 nm in many cases.

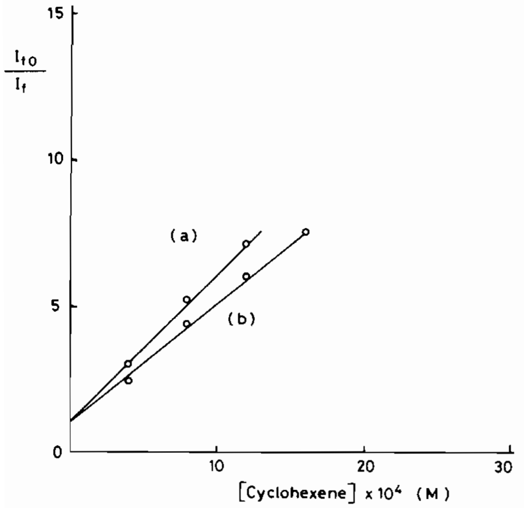

Fig. 3. Stern–Volmer plots of the intensity quenching of uranyl fluorescence at 493 nm with cyclohexene in aqueous solution at pH = 1: (a) 8.12×10^{-3} M UO_2^{2+}, (b) 8.12×10^{-3} M UO_2^{2+}, 8.08×10^{-3} M Mo(VI).

The difference spectra suggest that the species which disappears might be a heptamolybdate or octamolybdate moiety, since these are known to have $\lambda_{max} \approx 730$ nm and to be readily reoxidized in air [7, 9]. Nonetheless, we have a majority species that has a lower energy absorption maximum and is not sensitive to re-oxidation in air. This is surely a more highly condensed and/or protonated species [5], which may also incorporate uranyl molecules.

Of primary importance is the nature of the photoactive species. We consider that the uranyl ion is fundamentally responsible for the observed photochemistry. No reduced polymolybdate is produced under similar reaction conditions without UO_2^{2+}. Secondly, the polymolybdate(VI) does not quench the uranyl fluorescence and thus does not act as an energy transfer acceptor. UO_2^{2+} is therefore not serving simply as an 'antenna' for the polymolybdate. Although polymolybdate photooxidation of organic compounds has been documented [7], these systems require ultraviolet irradiation to be effective. We therefore conclude that the uranyl ion is the photoactive species.

However, it is certain that the polymolybdate(VI) changes the course of the uranyl/alkene reaction, since UO_2^{2+} alone does not oxidize alkenes in aqueous acid solutions [2b]. Moreover, typical uranyl photooxidations result in the loss of UO_2^{2+} and the production of U(IV) [1]; we observe instead that UO_2^{2+} is not consumed during the reaction. Thus, UO_2^{2+} acts as a photocatalyst in this system. This type of behavior of uranyl ions in the presence of a highly oxidized metal ion has been reported [2], but, to our knowledge, an alkene substrate has not been employed before in such a system*. It appears that the alkene oxidation reported by Sato and coworkers is also photocatalyzed by UO_2^{2+} [4]. However, these workers postulated that molecular oxygen was the electron-acceptor which prevented the permanent reduction of UO_2^{2+}; we are currently investigating the role of O_2 in our system. Thus, our system constitutes an original utilization of the uranyl ion for alkene photooxidation.

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*Preliminary experiments in our laboratory have indicated that mercury(II) and polytungstate(VI) can also be employed as electron acceptors in such a way.

The polymolybdate(VI) thus functions as a terminal electron acceptor in this system; the blue polymolybdate(V) is the proof of this. The weakly-reducing ($E^\circ = 0.062$ V *vs.* NHE) UO_2^+ species, which is thought to be the intermediate reduced form of the uranyl ion during photooxidation [1, 2], should be capable of reducing the polymolybdate(VI) [8]. However, we have also observed that U(IV) is able to effect this reduction. It is not completely clear whether the polymolybdate(VI) intervenes to oxidize the U(V) produced initially or the U(IV) produced by the disproportionation of U(V).

The linearity of the Stern–Volmer plots indicates that the UO_2^{2+}/cyclohexene quenching encounters are dynamic even with polymolybdate(VI) and thus that no UO_2^{2+}/cyclohexene pre-association occurs.

The smaller K_{sv} for cyclohexene in the presence of polymolybdate indicates that it is less effective in deactivating the uranyl ion excited state, even though the alkene oxidation is at the same time much more efficient. Since cyclohexene normally quenches UO_2^+ at nearly the diffusion-controlled limit [2], this decrease could be a diffusional effect due to the large size of the polymolybdate species.

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